6.2.3 Polyesters and Polyamides

There are two types of polymerisation: addition and condensation.

Addition Polymerisation

An addition polymer forms when unsaturated monomers react to form a polymer. Monomers contain C=C bonds.

Poly(alkenes) are chemically inert due to the strong C-C and C-H bonds and non-polar nature of the bonds and therefore are non-biodegradable.

Chain forms when same basic unit is repeated over and over.

You should be able to draw the polymer repeating unit for any alkene. For but-2-ene, the monomer with groups of atoms arranged around the double bond is shown.

Condensation Polymerisation

The two most common types of condensation polymers are polyesters and polyamides which involve the formation of an ester linkage or an amide linkage.

In condensation polymerisation there are two different monomers that add together and a small molecule is usually given off as a side-product e.g. H₂O or HCl.

The monomers usually have the same functional group on both ends of the molecule e.g. di-amine, di-carboxylic acid, diol, diacyl chloride.

Forming polyesters and polyamide uses these reactions we met earlier in the course:

<table>
<thead>
<tr>
<th>Reaction Type</th>
<th>Chemical Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carboxylic Acid + Alcohol</td>
<td>Ester + water</td>
</tr>
<tr>
<td>Acetyl chloride + Alcohol</td>
<td>Ester + HCl</td>
</tr>
<tr>
<td>Carboxylic Acid + Amine</td>
<td>Amide + water</td>
</tr>
<tr>
<td>Acetyl chloride + Amine</td>
<td>Amide + HCl</td>
</tr>
</tbody>
</table>

If we have the same functional group on each end of molecule we can make polymers so we have the analogous equations:

<table>
<thead>
<tr>
<th>Reaction Type</th>
<th>Chemical Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>dicarboxylic acid + diol</td>
<td>poly(ester) + water</td>
</tr>
<tr>
<td>diacyl dichloride + diol</td>
<td>poly(ester) + HCl</td>
</tr>
<tr>
<td>dicarboxylic acid + diamine</td>
<td>poly(amide) + water</td>
</tr>
<tr>
<td>diacyl dichloride + diamine</td>
<td>poly(amide) + HCl</td>
</tr>
</tbody>
</table>

Using the carboxylic acid to make the ester or amide would need an acid catalyst and would only give an equilibrium mixture. The more reactive acyl chloride goes to completion and does not need a catalyst but does produce hazardous HCl fumes.

Terylene- a common polyester

Terylene fabric is used in clothing, tire cords.

Using the benzene-1,4-dicarboxylic acid and ethane-1,2-diol, the polymerisation reaction produces the main polymer Terylene, which is a common polyester used in clothing and tire cords.

The -1 here is because at each end of the chain the H and OH are still present.

Using pentanediol dichloride and benzene-1,4-diol, the final reaction produces the main polymer Terylene, which is a common polyester used in clothing and tire cords.

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**Nylon 6,6 - a common polyamide**

\[
\begin{align*}
&n \begin{array}{c}
\text{C} \\
\text{OH}
\end{array} \rightleftharpoons \text{CO} \left(\text{CH}_2\right)_n \text{CO} \\
&n \begin{array}{c}
\text{H} \\
\text{N} \left(\text{CH}_2\right)_6 \text{N}
\end{array}
\end{align*}
\]

\[ \rightarrow \begin{array}{c}
\text{C} \\
\text{N} \left(\text{CH}_2\right)_n \text{N} \\
\text{H}
\end{array} \left(\text{CH}_2\right)_n \text{O} \left(\text{CH}_2\right)_n \text{O} + 2n-1 \text{H}_2\text{O}
\]

The 6,6 stands for 6 carbons in each of the monomers. Different length carbon chains produce different polyamides.

**Kevlar - a common polyamide**

\[
\begin{align*}
&n \begin{array}{c}
\text{C} \\
\text{OH}
\end{array} \rightleftharpoons \text{CO} \\
&n \begin{array}{c}
\text{H} \\
\text{N} \left(\text{CH}_2\right)_6 \text{N}
\end{array}
\end{align*}
\]

\[ \rightarrow \begin{array}{c}
\text{N} \\
\text{H}
\end{array} \left(\text{CH}_2\right)_n \text{O} \left(\text{CH}_2\right)_n \text{O} + 2n-1 \text{H}_2\text{O}
\]

**Note on classification for condensation polymers**

If asked for type of polymer: It is polyamide or polyester

Whereas type of polymerisation is condensation.

It is also possible for polyamides and polyesters to form from one monomer, if that monomer contains both the functional groups needed to react.

**4-hydroxybutanoyl chloride**

\[
\begin{align*}
\text{HO} & \left(\text{CH}_2\right)_2 \text{CO} \text{Cl} \\
\text{H}_2 & \text{N} \left(\text{CH}_2\right)_4 \text{N}
\end{align*}
\]

\[ \rightarrow \begin{array}{c}
\text{C} \\
\text{O}
\end{array} \left(\text{CH}_2\right)_3 \text{C} \left(\text{CH}_2\right)_3 \text{C} \left(\text{CH}_2\right)_3 \text{C} + 3 \text{H}_2\text{O}
\]

**2-hydroxypropanoic acid (lactic acid)**

\[
\begin{align*}
\text{H}_3 & \text{C} \left(\text{CH}_2\right)_2 \text{C} \text{OH} \\
\text{HO} & \text{CH} \text{C} \text{O}
\end{align*}
\]

\[ \rightarrow \begin{array}{c}
\text{C} \\
\text{O}
\end{array} \left(\text{CH}_2\right)_3 \text{C} \left(\text{CH}_2\right)_3 \text{C} \left(\text{CH}_2\right)_3 \text{C} + 3 \text{H}_2\text{O}
\]

"2 lactic acid molecules can also form a ring diester"

2 lactic acid molecules can also form a ring diester.

**4-hydroxypentanoic acid**

\[
\begin{align*}
\text{HO} & \text{CH} \text{C} \text{C} \text{CO} \\
\text{OH} & \text{H}_3 \text{C}
\end{align*}
\]

\[ \rightarrow \begin{array}{c}
\text{C} \\
\text{O}
\end{array} \left(\text{CH}_2\right)_3 \text{C} \left(\text{CH}_2\right)_3 \text{C} \left(\text{CH}_2\right)_3 \text{C} + 3 \text{H}_2\text{O}
\]

It is possible for some of these compounds to form various cyclic esters under different conditions from forming the polymer.

You do not need to learn these but may be asked to deduce structures from information given.
Chemical reactivity of condensation polymers

Polyesters and polyamides can be broken down by **hydrolysis** and are, therefore, biodegradable.

The reactivity can be explained by the presence of **polar bonds** which can attract attacking species such as nucleophiles and acids.

### Hydrolysis

Polyesters and polyamides can be hydrolysed by acid and alkali.

The hydrolysis will result in the original monomers forming - although the carboxylic acid or amine group will be in salt form depending on whether the conditions are alkaline or acidic.

$$\text{CO(CH}_2\text{)}_4\text{CONHC(CH}_3\text{)}_2\text{CH}_2\text{O}\rightarrow \text{H}_3\text{N}^+\text{H}_2\text{O} + \text{NH}_3^-$$

This polymer has both an amide and an ester link.

Condensation polymers may be photodegradable as the C=O bond absorbs radiation.